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ROTATIONAL SPECTROSCOPY OF

THE ALKALI FLUORIDES

by

Sidney Edwin Veazey

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Department of Physics
Duke University

Date: _____

Approved:

Walter Gordy, Supervisor

A dissertation submitted in partial fulfillment of
the requirements for the degree of Doctor of
Philosophy in the Department of Physics
in the Graduate School of Arts and
Sciences of Duke University

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ABSTRACT

(Physics)

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Rotational transitions of the alkali metal fluorides CsF , Rb^{87}F , Rb^{85}F , KF , NaF , and Li^7F have been experimentally measured in the millimeter and submillimeter wave regions where no previous measurements existed. The work was accomplished with a high temperature molecular beam microwave spectrometer which was previously utilized at Duke University for study of the alkali bromides, iodides, and chlorides. A more reliable oven was constructed and used to vaporize the alkali fluorides at temperatures up to 1100°C . Previously hot cell and molecular beam electric resonance techniques yielded the Dunham constants Y_{01} , Y_{11} , and Y_{21} by measurement of lower rotational transitions in the centimeter wave region. Present results with rotational transitions as high as $J = 27 \rightarrow 28$ and in the first three vibrational states gave Y_{01} , Y_{11} , and Y_{21} more accurately for the most part than previous measurements, and gave Y_{02} and Y_{12} for the first time. From these, the first four coefficients in Dunham's potential expansion, mass ratios of isotopes, Y_{10} and Y_{20} , moments of inertia, and internuclear distances were derived.

ACKNOWLEDGMENTS

I wish to sincerely thank Professor Walter Gordy for his direction and encouragement throughout the course of the research upon which this dissertation is based. The members of the microwave group repeatedly have given me valuable time, advice, and help on various problems which arose, and I am grateful for their assistance. Specifically I am indebted to Dr. P.L. Clouser for his help in starting the experiment and to E.F. Pearson for his aid in carrying this project through to its successful completion. I am deeply appreciative of the patience displayed by my wife during these last three years and of her help in the typing of this dissertation.

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S.E.V.

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ROTATIONAL SPECTROSCOPY OF
THE ALKALI FLUORIDES

INTRODUCTION

This dissertation describes the results of measuring pure rotational transitions in the first three vibrational states of the diatomic alkali metal fluorides CsF, Rb⁸⁷F, Rb⁸⁵F, KF, NaF, and Li⁷F. The transitions range from $J = 1 \rightarrow 2$ to $J = 27 \rightarrow 28$, and in frequency from 98 Gc/sec to 308 Gc/sec with accuracies better than 0.1 Mc/sec. The Dunham molecular structural constants, Y_{01} , Y_{11} , Y_{21} , Y_{02} , and Y_{12} , (corresponding to B_e , $-\alpha_e$, γ_e , $-D_e$, and $-\beta_e$ respectively) are deduced from the measured frequencies. From these constants, values for the moments of inertia, internuclear distances, isotopic mass ratios, vibrational constants Y_{10} and Y_{20} (ω_e and $\omega_e x_e$), and potential expansion coefficients have been obtained. The experimental results are significant because no rotational transitions higher than $J = 1 \rightarrow 2$ have been measured previously for the alkali fluorides.

The evolution of the present high temperature molecular beam microwave spectrometer allowed the possibility of measuring the alkali fluorides. Garrison and Gordy (1957) made the first successful measurements with the prototype of this spectrometer. They used a matched-horns type of cell and measured lines in the 90 Gc/sec to 100 Gc/sec range. Rusk and Gordy (1962)

extended the range of the spectrometer by changing to an S-band waveguide cell and using a higher frequency klystron. They measured the alkali bromides and iodides in the 90 to 200 Gc/sec range of the microwave region using an oven which was efficient to temperatures of about 800°C . Introduction of microwave lenses and high-pass microwave filters permitted another frequency extension to 312 Gc/sec in the study of the alkali chlorides. (Clouser and Gordy, 1964) The present spectrometer contains a new, more reliable oven which is capable of reaching a temperature of 1100°C and of responding rapidly to ordered temperature changes. Furthermore, the use of a persistent screen cathode ray oscilloscope and higher power klystrons now aid in the detection of weak lines.

There have been several types of spectrometers used to study the gaseous alkali halide molecules. The first of these was the infrared spectrometer which measured vibrational frequencies and obtained the molecular constants ω_e and $\omega_e x_e$. However, the precision of optical methods is less by several factors of ten than that available by microwave electronic means.

Secondly, C.H. Townes' Columbia University group (Honig et al., 1954) measured all of the alkali halides except LiF, NaF, KF, RbF, and LiCl with a "hot cell" microwave absorption spectrometer. Their measurements of CsF were in the 22 Gc/sec region and consisted of the $J = 1 \rightarrow 2$ transition in the lowest five vibrational states. Their spectrometer cell was a section of waveguide containing a Stark plate and the salt sample, all of which could be heated to a temperature of 930°C . Because of pressure and Doppler broadening and the limited range of frequencies (accurate to 1 part in 10^4), the

determinations of the molecular constants of CsF by the hot cell are less accurate and fewer in number than those derived from the present experiment.

Thirdly, the molecular beam electric resonance method has been employed to study the $J = 0 \rightarrow 1$ rotational transition of the remaining alkali fluorides. In this experiment, a beam from an oven is collimated and then passed through an inhomogeneous electric field A, a homogeneous electric field C with a superimposed microwave field, and finally another inhomogeneous electric field B. A stop-wire removes undeflected molecules from the beam, and a tungsten wire detector records a dip in the number of detected molecules at resonance. This occurs because the inhomogeneous fields deflect the molecules with equal but opposite forces by acting on the electric dipole moment. However if some molecules undergo a rotational transition in the C-field region, they are in a different quantum state as they traverse the B-field domain. Since the deflecting force depends on the quantum state, these molecules no longer experience the same deflection and do not reach the detector. Linewidths on the order of 40 kc/sec or better and accuracies of one part in 10^6 are reported. Limitations of the apparatus come from the insensitivity of molecules to Stark fields at high J transitions.

Thus it is evident that the present experiment offers distinct advantages over the three techniques described above. It is more accurate than infrared and hot cell measurements. It complements the molecular beam electric resonance techniques because many higher transitions may be studied.

It is the purpose of this thesis to present the new information gained

about the alkali fluorides. The first chapter describes the spectrometer in detail. Theoretical considerations are discussed in Chapter II, and the experimental results appear in the final chapter.

Chapter I

THE SPECTROMETER

The spectrometer may be divided into four principal subsystems: the cell and vacuum system, the oven, the microwave components, and the frequency measurement equipment. This chapter is devoted to the general layout of the spectrometer, a description of the subsystems in greater detail, and finally the procedures involved in making a "run".

The Cell and Vacuum System

A sketch of the cell and vacuum system appears in Figure 1. The cell is a 25 inch long section of copper S-band waveguide ($1 \frac{3}{8} \times 2 \frac{3}{4}$ inch internal cross-section). Attached to each end of S-band waveguide are 12 inch long G-band (0.075×0.034 inches) to S-band transition sections of electroformed copper. The small G-band end has a Scotch brand cellophane tape vacuum window which transmits microwave power very well. The larger end of the transition section contains the teflon microwave lens. The transition section achieves a vacuum seal to the S-band cell by means of an O-ring.

Figure 1. Sketch of the Cell and Vacuum Chamber

TO VACUUM PUMPS

THERMOCOUPLE GAUGE

IONIZATION GAUGE

TRANSITION SECTION

O-RING SEAL

WATER COOLED VACUUM BOX

TEFLON LENS

WATER COOLED S-BAND WAVEGUIDE

VACUUM WINDOW

OVEN

THERMOCOUPLE

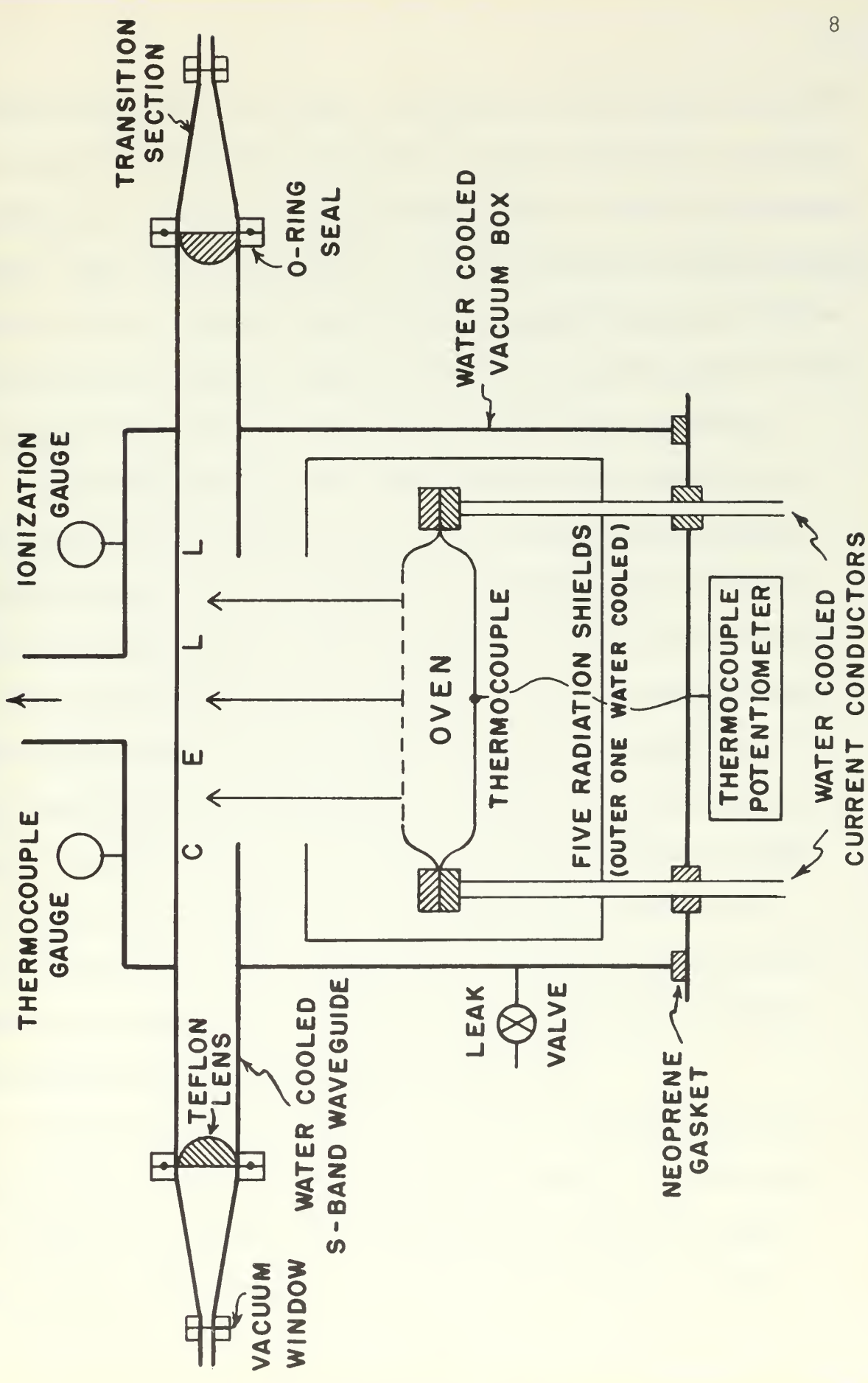
FIVE RADIATION SHIELDS (OUTER ONE WATER COOLED)

THERMOCOUPLE POTENTIOMETER

WATER COOLED CURRENT CONDUCTORS

LEAK VALVE

NEOPRENE GASKET



The middle six inches at the bottom small dimension of the S-band waveguide are cut away to allow entrance of the beam of sample and vacuum communication between the cell and the vacuum chamber. The cell penetrates the vacuum chamber, which is a box of dimensions 12 x 12 x 6 inches constructed of quarter inch brass plates. The bottom of the box is removable; it serves as a base for the oven and its radiation shields. A 6 x 12 inch neoprene gasket is used for a vacuum seal between the bottom plate and the vacuum chamber box.

A vacuum is obtained in the vacuum chamber box and cell by use of a water cooled diffusion pump backed up by a cold trap and two fore-pumps. The diffusion pump is a Consolidated Vacuum Corporation four inch oil diffusion pump model MCF-300. Between the diffusion pump and fore-pump is a cold trap which contains dry ice and acetone or liquid nitrogen depending on whether one wishes to trap out water or water and air, respectively. At first, there was only one fore-pump on the system, a Welch Duo-Seal vacuum pump model 1405. However, on some salts, water was released at temperatures near that of vaporization. In order to speed up evacuation of this water, a Central Scientific Co. Megavac pump was added in parallel to the Welch pump. Ordinarily only one fore-pump was used, the second being cut in when the need to increase pumping speed arose.

The fore-pump and dry ice and acetone cold trap operating alone will maintain a vacuum of approximately 10 microns. Vacuums up to one micron are measured by a National Research Corporation type 501 thermocouple vacuum gauge. With the diffusion pump and a liquid nitrogen cold trap

vacuums of 0.01 microns are typical. These vacuums better than one micron are measured by a Vacuum Electronic Manufacturing Corporation type RG 75P ionization gauge. The thermocouple and ion gauges are on the side and top of the oven box, respectively, and do not measure the pressure in the beam of salt. The vacuum will drop slightly as the oven is heated. How much it drops depends upon how long the system was outgassed and upon the temperature at which it was outgassed.

There is a leak valve on the side of the oven box to permit entrance of a test gas such as carbonyl sulfide. The necessity for this test and a discussion of this operation appear in the last section of this chapter.

The Oven

An indirectly heated oven described by Rusk (1962) was initially used to attempt temperatures up to 1000°C . Additional radiation shields with Babcock and Wilcox Company Kaowool brand ceramic fiber, and a change from Vycor glass heater element insulating tubes to ones of alumina ceramic all helped achieve this temperature. However, the oven was still not reliable at temperatures over 800°C , and about fifty per cent of the runs were aborted because of failure in the molybdenum wire heater elements or at their stainless steel connectors. Tantalum wire and a new type of connectors were tried, and they gave some improvement. Nevertheless, a hotter, more reliable oven was needed. A new

oven was designed such that changes in the spectrometer other than the oven power supply would be unnecessary.

A photograph of the new oven appears in Figure 2. The high temperature is produced by passing up to 350 amps through a thin walled stainless steel tube containing the salt sample. The tube is eleven inches long and is of either one inch O.D. and 0.010 inch wall thickness or 1 1/4 inch O.D. and 0.012 inch wall thickness. The former achieves temperatures of up to a maximum of 1100°C and it is shown in place in Figure 2. The latter reaches about 800°C , and an unfinished sample appears in the lower right hand side of Figure 2. For salts which vaporize below 800°C , the larger tube is used as it holds more sample, thereby permitting longer periods of vapor generation.

The tube has a six-inch row of closely spaced, one sixteenth inch diameter holes drilled along the middle section of the tube for effusion of the salt. Although these holes do not form a well-collimated beam of salt, line widths of from 150 kc/sec to 300 kc/sec are realized. The tube is crimped flat one inch from the end, loaded with salt, then crimped at the other end. The removable bottom of the vacuum chamber box serves as a base plate for the oven. As can be seen from Figure 2, the tube is clamped at each end by brass blocks which are supported by a pair of 5/16 inch copper pipes. The pair of copper pipes at each end carry water to cool the blocks as well as the current to heat the stainless steel tube. The copper pipes penetrate the base plate through epoxy resin insulators.

Figure 2. Photograph of the Oven and Radiation Shields



There are four stainless steel radiation shields which surround the oven tube. They are separated from the tube and each other by lavite and alumina ceramic spacers. A water cooled copper box with a stainless steel top completely surrounds the radiation shields except for an opening to permit efflux of the salt.

A chromel-alumel thermocouple is used to measure oven temperatures. It is insulated by alumina ceramic thermocouple insulating tubes and Flex-Sok steatite insulating beads, both from the Carborundum Company. The thermocouple measures the temperature at the outside surface near the center of the oven tube. The potentiometer used with the thermocouple is a Leeds and Northrup Company double-range potentiometer indicator No. 8657-C.

Control of the current through the oven tube was afforded by two type 136-2p ganged Superior Electric Company ^{variable autotransformers} ~~varies~~. The zero to 220 volts ^{autotransformers} ~~varies~~ from the ^{varies} was fed into a step-down transformer and reduced to about 5 volts. The transformer was initially a war surplus Navy Department, Bureau of Ships dry type single phase 440 volt to 220 and 110 step-down transformer built by Westinghouse. E.F. Pearson modified the transformer to produce the high current and low voltage required to heat the tube oven.

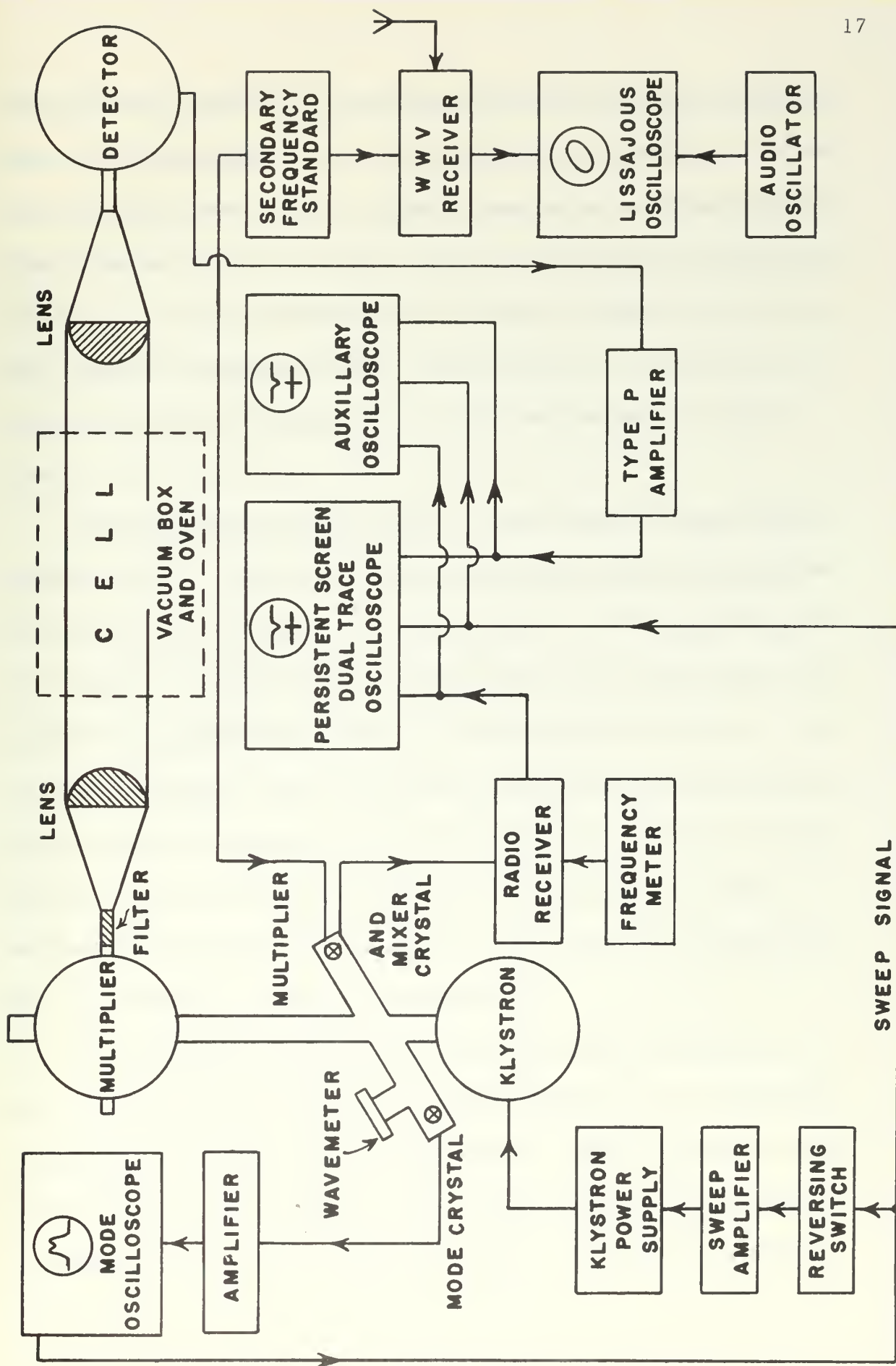
This oven was a significant improvement over the previous one because of its small mass. Once vapor generation began, one could quickly raise the temperature to increase line strength or lower it to conserve salt.

The Microwave System

The microwave system is shown schematically in Figure 3 with the frequency measurement equipment because of the interrelation of these two subsystems of the spectrometer. The source of microwave power is an OKI Electric Industry Co., Ltd. type 35V11 millimeter wave reflex klystron operating in the range 32 to 37 Gc/sec at a peak power of 150 MW. It is cooled by a water jacket which surrounds the body of the tube. Power from a type CVH constant voltage transformer built by the Sola Electric Company supplies the klystron power supply designed and built by D.F. Trippe for the Duke microwave laboratory. The sawtooth sweep voltage from the oscilloscope (Allen B. Dumont Laboratories type 208-B) used to display the klystron mode is amplified by the sweep amplifier, enters the klystron supply, and is superimposed on the klystron dc reflector voltage to electronically sweep the klystron. Since the klystron frequency is an approximately linear function of the reflector voltage, this frequency modulation produces a plot of power versus frequency on the mode and display oscilloscopes. A reversing switch is placed before the sweep amplifier to permit averaging the different time delays of the marker and the absorption trace.

Microwave power from the klystron enters J-band waveguide (0.276×0.124 inches) and travels to a J-band to G-band harmonic multiplier of the type described by King and Gordy (1954) and later modified by Burrus (1955). This differential screw and crossed waveguide mechanism brings a sharpened

Figure 3. Scheme of the Microwave and Frequency
Measurement Systems



two-mil tungsten cat whisker into contact with a doped silicon crystal supplied by Bell Laboratories. The cat whisker acts as an antenna to receive the fundamental power from the J-band waveguide and to reradiate harmonic power down the G-band waveguide. A dc bias arrangement permits biasing the contact such that maximum harmonic power is indicated at the detector. This multiplier supplied enough 8th harmonic power for observation of rotational transitions of wavelength less than a millimeter with video detection.

Harmonic power from the multiplier travels down the G-band waveguide and through a short straight-through G-band section or through one of four short filters designed to cut off the 4th, 5th, 7th, and 8th harmonics of the klystron at 32 Gc/sec. This procedure aids in the reduction of crystal noise by filtering out power of harmonics lower than that of the line being measured. Joining the filter is a G to S-band transition section. In the mouth of the transition section is lodged a teflon planoconvex lens constructed to focus the microwave power in a parallel beam down the S-band waveguide cell (Clouser and Gordy, 1964). On the other end of the cell is a similar lens and transition section.

Adjoining the second transition section is one of two detectors similar in construction to the multiplier except that there is only the G-band waveguide. One detector is a G-band detector with a cut off of 79 Gc/sec and the other is an F_2 band (J, G, and F_2 bands are Duke University designations) detector which cuts off at 140 Gc/sec. The detected signal is

amplified by a narrow-band, high-gain amplifier (M.I.T. Radiation Laboratory type P) before being sent to one vertical input of a dual-trace oscilloscope. At first the Tektronix Incorporated type 543 oscilloscope with a type CA dual-trace plug in unit was used for displaying the lines and markers. However, it was found that a persistent screen oscilloscope displayed weak lines more clearly. E.F. Pearson built a transistorized unit which converted a persistent screen oscilloscope (Dumont type 304A) for dual-tracing duty. This scope has a hood over it to further aid the eye for detection of weak lines. Since the hood prevents one from viewing the scope from afar, an auxilliary oscilloscope (Dumont 304H) is linked in parallel with the dual-trace scope. This also permits use of a Polaroid oscilloscope camera and gives a second experimenter a view of both line and marker.

In the J-band waveguide between the klystron and the multiplier are located a flap attenuator and a flap phase shifter (not shown in Figure 3). The first is used to reduce the power if lines appear power saturated, and the second can tune out klystron mode breaks. Also a Bethe-hole coupler draws off a small amount of power for mode display and frequency measurement. Sylvania IN26 crystals serve both purposes. A direct-reading cavity wavemeter (FXR Incorporated Model U410AF) allows measurement of the klystron frequency to within 10 megacycles by producing a visual "pip" in the mode display. A transistorized preamplifier boosts the mode signal before it reaches the mode scope.

Frequency Measurement

The primary frequency standard used for these measurements is the 5Mc/sec standard radio frequency broadcast from the National Bureau of Standards station WWV. National Bureau of Standards Miscellaneous Publication 236 reports that the frequency is normally held stable to one part in 10^9 at all times. The secondary frequency standard is essentially like the one described by Unterberger and Smith (1948) except that a 5 Mc/sec instead of a 10 Mc/sec basis is used. Customarily this secondary standard's crystal controlled oscillator is trimmed to about 100 cps above or below the exact 5 Mc/sec received from WWV (the WWV receiver is a Brown-Laboratories Incorporated WWV standard frequency calibrator). The 100 cps beat frequency from these two sources is compared to that of 100 cps from a calibrated test oscillator (Hewlett Packard model 650A) and monitored as a one to one Lissajous pattern on an oscilloscope. The audio oscillator is calibrated at 100 cps with a six to one Lissajous pattern by beating the 100 cps from the oscillator with the standard 600 cps broadcast by WWV. In the secondary standard the 5 Mc/sec ($\pm \sim 100$ cps) is doubled, tripled, and tripled again to 90 Mc/sec. The 90 Mc/sec is amplified and tripled and the resulting 270 Mc/sec fed into the input resonator of a double cavity klystron. The output resonator is tuned to 2970 Mc/sec and this frequency is mixed with some 90 Mc/sec and sent to a Sylvania IN26 silicon crystal multiplier in one arm of the Bethe-hole coupler. Here, not only are

harmonics of 90 and 2970 Mc/sec produced, but these harmonics mix with the klystron frequency. Hence markers appear every 90 megacycles and beat note markers are produced by a radio receiver (Hallicrafters Company model SX-42). Since the klystron sweep is synchronized with the dual-trace oscilloscope displays, measurement of the receiver setting when the marker is aligned with the detected absorption gives the positive or negative frequency difference from an integral multiple of 90 Mc/sec. The receiver dial gives a rough indication of this frequency difference, but it is measured precisely with a direct reading VHF frequency meter (Gertsch Products Incorporated Model FM-3, which is accurate to 0.001% in its 20 to 40 Mc/sec tuning range). The decision as to which integral multiple of 90 Mc/sec is appropriate is made by a reading of the wavemeter previously described and located on the other arm of the Bethe-hole coupler.

To summarize frequency measurement the following equation is presented:

$$\nu = [N(90) \pm R \pm 18ND] k \quad (1)$$

The sign of the receiver reading R is determined as follows: With the reversing switch on forward sweep, the receiver is tuned to higher frequencies. If the marker moves to the right (toward higher frequencies) on the oscilloscope display, it is termed positive. That is, the marker is the beat note produced by a multiple N of 90 Mc/sec (discovered from the wave meter reading) and a klystron frequency higher by R than this multiple. Conversely, a negative marker, produced by a beat note from a klystron frequency lower by R than the multiple N of 90 Mc/sec, moves to the left on the display as

the receiver is tuned to higher frequencies. For positive markers the multiple of 90 Mc/sec below the klystron frequency is used and R as determined by the receiver and frequency meter is added to this multiple. In the last term, the 18 is the multiplier of 5 Mc/sec to reach the 90 Mc/sec. The D term is the difference between the secondary frequency standard 5 Mc/sec $\pm D$ and the WWV signal of exactly 5 Mc/sec. As noted before, the frequency standard is trimmed to a D of nearly 100 cps above or below WWV, because the audio oscillator is easily calibrated at this frequency. Here the correct sign of D is determined by measurement of a known line of a test gas. During a "run", the D is monitored before and after each measurement, but it seldom changes more than half a cycle during an entire "run". Lastly, the exact klystron frequency inside the bracket in Equation (1) is then multiplied by the klystron harmonic k to obtain the frequency of the line.

Experimental Procedure

The new oven has reduced the experimental cycle time from two days down to one day. On occasion two "runs" have been made in one twenty-four hour period. The reason for this saving in time comes from the rapid cooling of the new oven because of its small mass and the water-cooled clamp heat sinks at each end of the oven. Since sometimes only one line may be located and measured during the twenty to forty-five minutes of salt vapor generation, this saving is significant.

Before the experimental cycles are started, a literature search for

data on the molecule to be investigated is made. These data consist of melting temperatures, dipole moments, the Dunham constants Y_{01} , Y_{11} , and Y_{21} from molecular beam electric resonance and hot cell measurements, and Y_{10} from infrared techniques. A fairly accurate value of Y_{02} may be calculated from the available Y_{01} and Y_{10} as shown in Equation (24). These constants are employed in the calculation of the approximate line frequencies, klystron frequencies, receiver readings, and absorption coefficients by two computer programs described in Chapter II.

The cycle begins with the loading of the tube with salt. For hygroscopic CsF, RbF, and KF it is necessary to load the tube with anhydrous samples in a dry box with phosphorus pentoxide as a desiccant. A high temperature reaction of the type $\text{KF} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{HF}$ necessitates the exclusion of water by this procedure. Next the tube, radiation shields, spacers, thermocouple, and oven base are assembled and quickly raised into the vacuum box. The fore pump is started and the cold trap filled with a dry ice-acetone mixture. When the vacuum reaches 100 microns, the cooling water, diffusion pump, and oven are turned on. Usually the oven is set for roughly 300°C , and the system is left to outgas overnight.

The next morning the microwave sensitivity is checked and more often than not several new detector contacts must be tried before sufficient sensitivity is obtained. Although it sometimes takes several days to achieve a desirable multiplier contact, such contacts often last for months. These multiplier and detector contacts consist of touching the cat whisker to a sensitive

spot on a crystal with just the right pressure. After a couple of unsuccessful tries, the cat whisker is resharpened by electrolytic etching in a sodium hydroxide solution and examined under a microscope before reassembly.

Once apparently good contacts have been made, one tests them by observing transitions of a test gas such as carbonyl sulfide (OCS). This linear molecule has many transitions in the microwave region, and one can usually find a transition near that of a salt line he wishes to measure. In addition, this gas has the advantage of a harmonic series at a 36.48 Gc/sec klystron frequency. This allows third through tenth harmonic transitions to be observed on the oscilloscope simultaneously, if the contacts are adequate.

When the desired microwave sensitivity is achieved, the dry ice Dewar vessel on the cold trap is replaced by one with liquid nitrogen. One next tunes to obtain a strong marker where the line to be measured is expected to appear. The oven is brought to salt vaporization temperature, and the system is tuned until the line is discovered. If any doubt exists as to which of two closely spaced lines (of different klystron harmonics) is being measured, application of several filters of known cutoff will usually resolve the indecision. Sometimes weak lines are strengthened when the pumps are closed off and the pressure allowed to rise slightly. This procedure scatters salt molecules into the ends of the cell thereby producing a longer absorption path length. Three or more measurements at both forward and reverse klystron sweep are made. The wavemeter settings, receiver readings, frequency meter readings, frequency standard differences, and oven temperatures are

recorded. A Polaroid oscilloscope camera records the oscilloscope trace. Then if there is more salt left, the oven temperature is quickly reduced below the vapor generation point until the system is tuned for the next transition's measurement when the salt is exhausted, the system is cooled, dismantled, cleaned, and readied for the next cycle.

Chapter II

THEORY

The Diatomic Molecule

The energy of the diatomic molecule may be considered to consist of three basic parts in addition to its linear kinetic, nuclear, and rest energy. These three contributions are the rotational, vibrational, and electronic energies, in order of increasing energy. Pauling and Wilson (1935), using the arguments of Born and Oppenheimer (1927), discuss the separation of the electronic from the rotational and vibrational solutions. This is possible because the light electrons quickly readjust to an equilibrium state for each position of the rotating and vibrating nuclei. Because the electronic transition-frequencies lie far beyond the microwave region in the optical region, only the electronic ground state is important at the temperatures of this experiment.

The time-independent Schrödinger wave equation for a nonrigid rotor of masses m_1 and m_2 may be written in spherical polar coordinates as

$$\frac{h^2}{8\pi^2 \mu r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \varphi^2} \right] + V(r)\Psi = E\Psi, \quad (2)$$

where μ is the reduced mass $\frac{m_1 m_2}{m_1 + m_2}$, and h is Planck's constant.

(Townes and Schawlow, 1955) Separation is effected by the substitution

$$\Psi = R(r) \Theta(\theta) \Phi(\varphi).$$

The solutions for $\Theta(\theta)$ and $\Phi(\varphi)$ are the rigid rotor solutions which occur only when the energy eigenvalues

$$E = \frac{h^2}{8\pi^2 I} J(J+1), \quad (3)$$

where J is a positive, integral, rotational quantum number, and I is the molecular moment of inertia. Defining

$$B_e = \frac{h^2}{8\pi^2 I_e}, \quad (4)$$

applying the selection rule for absorption $\Delta J = +1$, and invoking Bohr's postulate, one obtains a transitional frequency of

$$\nu = \frac{E_{J+1} - E_J}{h} = 2B_e(J+1) \quad (5)$$

for the rigid rotor.

The remaining radial wave equation depends on the form of $V(r)$.

Pekeris (1934) has solved this equation using the highly successful Morse potential (Morse, 1929)

$$V(r) = D \left[1 - e^{-a(r-r_e)} \right]^2 \quad (6)$$

for any value of J . In the Morse potential, D is the dissociation energy, r_e the equilibrium internuclear distance, and the constant a is to

be determined. Herzberg (1950) gives the number of terms necessary to analyze the present data:

$$E_{J,v}/h = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \dots \quad (7)$$

where

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2}\right) + \gamma_e \left(v + \frac{1}{2}\right)^2 + \dots \quad (8)$$

$$D_v = D_e + \beta_e \left(v + \frac{1}{2}\right) + \dots \quad (9)$$

and H_v may be approximated by

$$H_v \sim H_e = \frac{2D_e}{3\omega_e^2} (12B_e^2 - \alpha_e \omega_e) . \quad (10)$$

Here ω_e is the vibrational frequency of a simple harmonic oscillator, and $\omega_e x_e$ is the anharmonic correction term. B_e is the term associated with the rigid rotor, which is corrected for vibration by the α_e and γ_e terms to form B_v . Similarly D_e is the centrifugal stretching term, and vibrational interaction necessitates the correction term β_e .

A more accurate potential function is the one used by Dunham (1932b). He expanded about the equilibrium internuclear distance r_e in a power series of the form

$$V(\xi) = ha_0 c \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots) \quad (11)$$

where $\xi = \frac{r - r_e}{r_e}$ and a_0 is described by Equation (27). Dunham used

the Wentzel-Kramers-Brillouin method to get the eigenvalues of Schrödinger's equation. (Dunham, 1932a) The energy level equation so obtained may be written in the following form:

$$\frac{E_{J,v}}{h} = \sum_{\ell m} Y_{\ell m} \left(v + \frac{1}{2}\right)^{\ell} J^m (J+1)^m, \quad (12)$$

which when expanded reads

$$\begin{aligned} \frac{E_{J,v}}{h} = & Y_{10} \left(v + \frac{1}{2}\right) + Y_{20} \left(v + \frac{1}{2}\right)^2 + Y_{01} J(J+1) \\ & + Y_{11} \left(v + \frac{1}{2}\right) J(J+1) + Y_{12} \left(v + \frac{1}{2}\right) J^2 (J+1)^2 \\ & + Y_{02} J^2 (J+1)^2 + Y_{21} \left(v + \frac{1}{2}\right)^2 J(J+1) \\ & + Y_{03} J^3 (J+1)^3 + \dots \end{aligned} \quad (13)$$

When one applies the rotational absorption selection rules $\Delta J = +1$, $\Delta v = 0$ to Bohr's postulate, one obtains a transition frequency of

$$\begin{aligned} \nu = \frac{E_{J+1,v} - E_{J,v}}{h} = & 2Y_{01} (J+1) + 2Y_{11} \left(v + \frac{1}{2}\right) (J+1) \\ & + 2Y_{21} \left(v + \frac{1}{2}\right)^2 (J+1) + 4Y_{02} (J+1)^3 \\ & + 4Y_{12} \left(v + \frac{1}{2}\right) (J+1)^3 + Y_{03} (J+1)^3 \\ & [(J+2)^3 - J^3] + \dots \end{aligned} \quad (14)$$

By comparison of Equations (7), (8), (9), and (13) it is seen that the following relations hold to first order:

$$\begin{aligned}
 Y_{10} &\sim \omega_e & Y_{20} &\sim -\omega_e x_e \\
 Y_{01} &\sim B_e & Y_{11} &\sim -\alpha_e \\
 Y_{02} &\sim -D_e & Y_{21} &\sim \gamma_e \\
 Y_{03} &\sim H_e & Y_{12} &\sim -\beta_e
 \end{aligned} \tag{15}$$

These approximations are usually adequate except for Y_{01} , for which the accuracy of microwave measurements warrants the expression

$$Y_{01} = B_e \left(1 + \frac{B_e^2 \beta_{01}}{\omega_e^2} \right), \tag{16}$$

where

$$\beta_{01} = Y_{10}^2 Y_{21} / 4Y_{01}^3 + 16a_1 Y_{20} / 3Y_{01} - 8a_1 - 6a_1^2 + 4a_1^3 \tag{17}$$

and a_1 is given by Equation (28). (Dunham, 1932b; Townes and Schawlow, 1955)

Some of the Y 's which will be necessary for the data analysis are repeated from Dunham's paper for convenience (Terms negligible for present purposes have been dropped.):

$$Y_{00} = \left(\frac{B_e}{8} \right) \left(3a_2 - \frac{7}{4}a_1^2 \right) \tag{18}$$

$$Y_{10} = \omega_e [1 + \dots] \quad (19)$$

$$Y_{20} = B_e / 2 [3(a_2 - 5a_1^2/4) + \dots] \quad (20)$$

$$Y_{01} = B_e [1 + (B_e^2 / \omega_e^2) (15 + 14a_1 - 9a_2 + 15a_3 - 23a_1 a_2 + 21(a_1^2 + a_1^3)/2)] \quad (21)$$

$$Y_{11} = B_e^2 / \omega_e [6(1 + a_1) + \dots] \quad (22)$$

$$Y_{21} = (6B_e^3 / \omega_e^2) [5 + 10a_1 - 3a_2 + 5a_3 - 13a_1 a_2 + 15(a_1^2 + a_1^3)/2] \quad (23)$$

$$Y_{02} = - (4B_e^3 / \omega_e^2) [1 + \dots] \quad (24)$$

$$Y_{12} = - (12B_e^4 / \omega_e^3) (19/2 + 9a_1 + 9a_1^2/2 - 4a_2) \quad (25)$$

$$Y_{03} = 16 B_e^5 (3 + a_1) / \omega_e^4 \quad (26)$$

$$a_0 = (\omega_e^2 / 4B_e) c \quad (27)$$

$$a_1 = (Y_{11} Y_{10} / 6Y_{01}^2) - 1. \quad (28)$$

Now, solving Equations (25), (23), and (24) respectively one gets

$$a_2 = Y_{12} \omega_e^3 / 48 B_e^4 + 19/8 + 9/4 a_1 + 9/8 a_1^2, \quad (29)$$

$$a_3 = \omega_e^2 Y_{21} / 30 B_e^3 - 1 - 2 a_1 + 3/5 a_2 + 13/5 a_1 a_2 - 3/2 (a_1^2 + a_1^3), \quad (30)$$

and

$$\omega_e = 2 (B_e^3 / Y_{02})^{1/2}. \quad (31)$$

From the definition of B_e , one finds that

$$I_e = \frac{h}{8 \pi^2 B_e} = 505587.4 / B_e \text{ amu } \text{\AA}^2, \quad (32)$$

where B_e is expressed in Mc/sec, (Gordy, Smith, and Trambarulo, 1953) and $h = h/2\pi = 1.05443 \pm 0.00004 \times 10^{-27}$ erg-sec. (Dumond and Cohen, 1958) From I_e , r_e may be calculated from the equation

$$r_e = (I_e / \mu)^{1/2} \text{ \AA}, \quad (33)$$

where the reduced mass μ is in amu.

One can often obtain formulas in more common nomenclature by substituting for the potential coefficients. Herzberg (1950) gives the useful formula

$$\beta_e = D_e \frac{8 \omega_e x_e}{\omega_e} - \frac{5 \alpha_e}{B_e} - \frac{\alpha_e^2 \omega_e}{24 B_e^3} \quad (34)$$

by which $\omega_e x_e$ may be calculated. He also lists another important formula shown by Pekeris to be valid for the Morse potential:

$$\alpha_e = 6 \frac{(\omega_e x_e B_e^3)^{\frac{1}{2}}}{\omega_e} - 6 B_e^2 / \omega_e . \quad (35)$$

The use of all these equations will be amplified in the following material.

Isotopes

Quite accurate mass ratios may be deduced from microwave measurements of two isotopic molecules, under the reasonable assumption that the potential function is the same for the two molecules. Additionally, one may obtain the molecular constants of one isotopic species (primed) from the constants of another species (unprimed) with the relation given by Dunham (1932 b):

$$\frac{Y'_{lm}}{Y_{lm}} = \left(\frac{\mu}{\mu'} \right)^{\frac{l}{2} + m} \quad (36)$$

which is good to first order. Hence, defining ρ to be the square root of the ratio of the reduced masses $\left(\frac{\mu}{\mu'} \right)^{\frac{1}{2}}$, and substituting the practically synonymous band spectrum terms one obtains the relations (see Herzberg, 1950):

$$\begin{array}{lll} \omega'_e = \rho \omega_e & B'_e = \rho^2 B_e & \alpha'_e = \rho^3 \alpha_e \\ \omega_e x'_e = \rho^2 \omega_e x_e & D'_e = \rho^4 D_e & \gamma'_e = \rho^4 \gamma_e \\ \beta'_e = \rho^5 \beta_e & Y'_{00} = Y_{00} & \end{array} \quad (37)$$

Taking into account the higher order terms, Dunham obtains

$$\frac{Y'_{lm}}{Y_{lm}} = \left(\frac{\mu}{\mu'}\right)^{l/2+m} \left[1 + \frac{\beta_{lm} B_e^2}{\alpha_{lm} \omega_e^2} \left(\frac{\mu - \mu'}{\mu'}\right) \right], \quad (38)$$

where the Y_{lm} 's are written in the form

$$Y_{lm} = f_{lm}(B_e, \omega_e) [\alpha_{lm} - (B_e^2/\omega_e^2) \beta_{lm} + \dots]. \quad (39)$$

The present measurements require these additional terms for Y_{01} ; and Y_{01} and β_{01} appear in Equations (16) and (17) (α_{lm} is one, and $f_{lm}(B_e, \omega_e)$ is simply B_e in this case).

Following Honig et al., (1954)

$$\frac{\mu}{\mu'} = \frac{B'_e}{B_e} = \frac{Y'_{01}}{Y_{01}} \left[1 + \beta_{01} \frac{B_e^2}{\omega_e^2} \left(\frac{\mu}{\mu'} - 1\right) \right]^{-1}; \quad (40)$$

whereupon

$$\frac{m_1}{m'_1} = \frac{(m_2/m'_1)(B'_e/B_e)}{1 + m_2/m'_1 - B'_e/B_e}. \quad (41)$$

Also they list the fractional error as

$$\pm \left[\delta \frac{m_2/m'_1 + 1}{\left(\frac{\mu}{\mu'}\right)(m_2/m'_1 + 1 - \frac{\mu}{\mu'})} \pm \frac{\Delta(1 - \frac{\mu}{\mu'})}{(m_2/m'_1)(m_2/m'_1 + 1 - \frac{\mu}{\mu'})} \right], \quad (42)$$

where Δ is the fractional error in the common mass m_2 and δ is the fractional error in $\frac{\mu}{\mu'}$.

Sensitivity

There are many factors which affect the detection sensitivity of the observed transitions. First, of course, are the conditions imposed by the apparatus. The klystron varies in power output over its range. The power available from the harmonic generator decreases monotonically with increasing harmonics. The contacts on the multiplier and detector vary as to quality, and the mechanical and electronic tuning settings are never identical over the wide range of measured frequencies. Nevertheless, accepting the above variables, and considering the cell absorption path to contain the same number of molecules for each salt sample and measurement, some pertinent observations about sensitivity may be made from several theoretical and experimental considerations.

The fraction of molecules in a given vibrational state v is expressed by the formula (Gordy et al., 1953)

$$F_v = \frac{e^{-v h \omega_e / kT}}{Q_v} \quad (43)$$

where k is Boltzmann's constant and Q_v is the partition function

$$Q_v = \sum_{n=0}^{\infty} e^{-h(n_1 \omega_1 + n_2 \omega_2 + \dots) / kT} \quad (44)$$

This reduces for the case of only one vibrational frequency to

$$F_v = e^{-vh\omega_e/kT} (1 - e^{-h\omega_e/kT})^{-1} \quad (45)$$

There is one advantage in the high temperature T (see Table I) necessary to produce the alkali fluoride vapors; greater populations in the higher vibrational states are achieved.

Similarly, the fraction of molecules in a given rotational state is given by the relation

$$F_J = (2J + 1) \frac{hB}{kT} e^{-hBJ(J+1)/kT} \quad (46)$$

where $2J + 1$ is the degeneracy and kT/hB is an approximation for the rotational partition function. Here too, the population in the higher rotational states is enhanced by the high temperature.

The peak absorption coefficient α is expressed by

$$\alpha = \frac{8\pi^2 \nu_0^2 N F_v F_J |\mu_{ij}|^2}{3ckT \Delta\nu} \quad (47)$$

for plane polarized radiation where ν_0 is the resonant frequency, N is the number of molecules per unit volume in the absorption cell, $\Delta\nu$ is the halfwidth of the line, and $|\mu_{ij}|^2$ is the dipole moment matrix element squared which is $\mu^2(J+1)$ (see Gordy et al., 1953; Townes and Schawlow, 1955). This yields an expression for α of the form

$$\alpha = \frac{8\pi^2 N h}{3ck^2 \Delta\nu} \left[\frac{\mu^2 \nu^3}{T^2} e^{-vh\omega_e/kT} e^{-hBJ(J+1)/kT} (1 - e^{-h\omega_e/kT}) \right] \quad (48)$$

Table I
Oven Temperature Required to Vaporize
the Alkali Fluorides

Alkali Fluoride	Oven Temperature ^a in °C
CsF	650
RbF	720
KF	800
NaF	980
LiF	950

a. These values varied slightly with different placement of the thermocouple. Extreme accuracy was not the goal, but it was helpful to know at which temperature to expect vapor generation of sufficient pressure to detect transitions. These temperatures were recorded at the onset of vapor generation. However, temperatures were raised as much as 100°C to strengthen weak lines.

in the region near $\nu = \nu_0$.

The dipole moments μ of the alkali fluorides are very high (see Table II). Herein lies the first explanation for the strong absorption coefficient encountered in this experiment. These large dipole moments more than offset the $1/T^2$ temperature factor when one makes comparison to typical gases at room temperature with dipole moments of one Debye or less. Secondly, the ν^3 factor in the expression for the absorption coefficient gives much greater absorption at 100 to 300 Gc/sec than at the relatively low frequencies of the hot cell and molecular beam electric resonance methods. Thirdly, the low pressure and reasonable molecular beam serve to reduce the line width and hence increase the absorption coefficient relative to that of hot cell techniques. Lastly, the natural populations of the higher rotational levels are greater than the lower ones, which is an additional advantage when one measures in the millimeter and submillimeter region.

There are other factors peculiar to particular molecules which serve to reduce the absorption. The first of these is a division into isotopic species which simply reduces the number of molecules available for a given species' transitions. Secondly, for some alkali fluorides a four-atom dimer molecule can exist as well as the diatomic molecule. This formation of dimers appears to be greater for the lighter alkali fluorides, as evidenced by the weak observed lines in sodium fluoride and yet weaker lines in lithium fluoride. Eisenstadt, Rothberg and Kusch (1958)

Table II
Dipole Moments

Alkali Fluoride	Dipole Moment in Debye ^a
CsF	7.874 ^b
Rb ⁸⁵ F	8.80 ^c
KF	8.60 ^d
NaF	8.19 ^e
Li ⁷ F	6.6 ^f

a. These values are either the equilibrium dipole moment μ_e or the dipole moment in the zeroth vibrational state μ_0 .

b. Honig et al., (1954).

c. Lew et al., (1958).

d. Green and Lew, (1960).

e. Bauer and Lew, (1964).

f. Braunstein and Trischka, (1955).

studied the dissociation energies of the LiF, NaF, KF, RbF and CsF dimers and found them to be 58.9, 54.3, 47.6, 42.0, and 37.8 k cal/mole, respectively. They also observed a lithium fluoride trimer and noted that the abundance of the dimer increases in the sequence CsF to LiF. There are other experimental evidences for large concentrations of dimers in lithium fluoride in particular and in the lithium halides in general, e.g. Schoonmaker and Porter, (1959) and Berkowitz, (1958).

Table III presents calculations and experimental determinations for several of these earlier discussed characteristics affecting sensitivity.

Analysis of Data

The major data analysis was accomplished on the IBM 7072 digital computer in the Duke University Digital Computing Laboratory, with the remainder being done on a desk calculator. First an auxiliary program was used to calculate the expected line frequencies according to Equation (14) without, however, the small term in Y_{03} . Previous data comprising Y_{01} , Y_{11} , and Y_{21} were used. Theoretical estimates according to Equation (25) were used for Y_{02} . Once a solution for the Y_{lm} 's was made, these new values (now including Y_{12}) were inserted into the program the better to pinpoint lines for future measurement. The program computed all J transitions in the first four vibrational states within the measurement capabilities of the spectrometer. In addition, the program output

Table III
Spectral Absorption Characteristics

Molecule	F_J Rotational state fraction of transition nearest 200 Gc/sec	F_v Vibrational state fraction			
		$v = 0$	$v = 1$	$v = 2$	$v = 3$
CsF	0.0093	0.44	0.25	0.14	0.08
Rb ⁸⁷ F	0.0085	0.42	0.24	0.14	0.08
Rb ⁸⁵ F	0.0085	0.42	0.24	0.14	0.08
KF	0.0077	0.39	0.24	0.14	0.09
NaF	0.0067	0.43	0.25	0.14	0.08
Li ⁷ F	0.0051	0.67	0.21	0.07	0.02

Table III. (continued)

Absorption coefficient $\alpha_{J,0}$ of transition nearest 200 Gc/sec in $v=0$ state ($\frac{8\pi^2Nh}{3ck^2\Delta\nu} \times 10^{12}$ /unit length)	Isotopic percentage	Dimer to monomer ratio ^a	Trimer to monomer ratio ^a
0.25	100.	0.29	0.0022
0.23	27.8	0.59	0.0055
0.23	72.2	0.59	0.0055
0.17	100.	0.93	0.013
0.14	100.	0.80	0.015
0.08	92.6	3.3	0.31

a. Schoonmaker and Porter, (1959).

gave the quantum numbers, the klystron frequencies, the harmonics, and the expected receiver readings. This program was extremely valuable in that it saved many hours at the desk calculator and made assignment of quantum numbers to a measurement a simple task.

A second program calculated the fraction of molecules in each vibrational state, each rotational state, and the absorption coefficient for each transition. This served as an aid in the determination of the transitions for which to search and in the estimate of the sensitivity necessary for detection of these transitions.

The majority of the data reduction was done with computer programs written and described by P.L. Clouser (1963). Before the measured frequencies ν_i were processed, they were corrected by subtraction of the last term in Equation (14), which is quite small. The Y_{03} or H_e constant is approximated by Equation (10) and the coefficient $(J+1)^3 [(J+2)^3 - J^3]$ is taken from an output table of these values prepared by the computer. Then n ($n \geq 5$) corrected measured frequencies ν_i' appear in the form

$$\begin{aligned} \nu_i' = \nu_i - (J+1)^3 [(J+2)^3 - J^3] Y_{03} = & 2(J+1) Y_{01} + 2(J+1)(\nu + \tfrac{1}{2}) Y_{11} \\ & + 2(J+1)(\nu + \tfrac{1}{2})^2 Y_{21} + 4(J+1)^3 Y_{02} + 4(J+1)^3 (\nu + \tfrac{1}{2}) Y_{12} . \end{aligned} \quad (49)$$

These n equations are reduced to five normal equations in the five unknown Y_{lm} 's. These normal equations are constructed to minimize the errors squared and summed. These five equations are then solved for

the Y_{lm} 's.

Errors

It is believed that the measuring procedure outlined in Chapter I removes systematic errors from the measurements. The frequency meter accuracy is such that maximum errors of 0.004 Mc/sec would occur at the highest transitional frequencies. This is well within the dispersion of the measurements, and hence the accuracy is limited solely by the ability of the experimenter to visually align the marker and the transition's "pip" on the oscilloscope. These random human errors may be treated statistically.

The errors of each Y_{lm} are computed in the manner described by Topping (1956). First the difference d_i between the measured frequencies and the calculated frequencies computed from the new Y_{lm} 's is obtained. Then the standard error α of the frequencies is defined by

$$\alpha = \sum_i d_i^2 / (n - 5) \quad (50)$$

where 5 is the number of unknowns. As many lines as practical are measured to increase n and hence reduce the standard error. Actually each line is measured at least three times and in most cases more than three times. These three or more measurements are averaged and recorded as the measured line frequency. Finally the error for each Y_{lm} is described by

the equation

$$\alpha_{lm} = [(\Delta_{lm} / \Delta) \alpha^2]^{\frac{1}{2}} \quad (51)$$

where Δ is the determinant of the coefficients and Δ_{lm} is the minor of the Y_{lm} in the set of normal equations.

The other constants are calculated in a straight forward manner by use of the equations discussed at the beginning of this chapter. In the process, an iteration procedure is used to achieve a better solution for B_e after Y_{01} is initially set equal to B_e in the parenthetical quantity of Equation (16). Errors of the derived constants come from a first differential of the equation for the derived constant in terms of the measured constants and their errors.

Chapter III

RESULTS

Measured and Calculated Frequencies and the Dunham Constants

In Tables IV through IX are recorded the measured frequencies and the frequencies calculated from the new Y_{lm} rotational constants. The measured frequencies have been corrected for the small Y_{03} term. Also the calculated frequency has been determined from Equation (14) without the Y_{03} term so that comparison with the measured frequencies will be more realistic. The five Y_{lm} 's (Y_{01} , Y_{11} , Y_{21} , Y_{02} , and Y_{12}) computed from these corrected measured frequencies are listed in Table X. These five constants are termed the measured constants, whereas the other Y_{lm} 's and all of the other information in this chapter are calculated from these measured Y_{lm} 's.

Cesium fluoride. Cesium fluoride is the heaviest of the molecules studied, and as such it has the most transitions within the range of the spectrometer. The nineteen measured transitions for this molecule comprise the largest set of measurements, and this set includes the only measurement in the third vibrational state. Referral to Table III shows that cesium fluoride

has the largest absorption coefficient. Cesium has only one isotope, and cesium fluoride has the smallest dimer to monomer and trimer to monomer ratios of any of the alkali fluorides. These factors combine to produce the most easily detectable and measurable transitions of this series. Figure 4(a) shows the oscilloscope photographs of the $J = 12 \rightarrow 13$ rotational transitions in the three lowest vibrational states. Figure 5(c) gives the trace of the $J = 27 \rightarrow 28, v = 0$ transition. This transition has the highest measured frequency at 308,009.147 Mc/sec.

The five rotational structure constants derived from a solution of these nineteen measurements appear in Table X (the J quantum number is always the lower state of the transition). C.H. Townes' Columbia University group measured the cesium fluoride transition $J = 1 \rightarrow 2$ in the first five vibrational states. (Honig et al., 1954) The accuracy of their measurements is one part in 10^4 , whereas the present measurements are accurate to one part in 10^6 . The values of Y_{01} , Y_{11} , and Y_{21} are an order of magnitude more accurate than those obtained from these hot cell measurements (see Table XI). There is agreement within the stated errors on the Y_{01} term, but there is disagreement on the Y_{11} and Y_{21} terms. This discrepancy may have arisen because Honig et al., used Barrow and Caunt's value of ω_e to estimate D_e (see Table XIII). Similar discrepancies were noted by Rusk (1961) and Clouser (1963) in comparing alkali bromide, iodide, and chloride data from this spectrometer and the hot cell spectrometer of Townes' group. As for all of the alkali fluorides, Y_{02} and Y_{12} have been experimentally determined

Table IV
Transition Frequencies of CsF

J	v	Measured frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
8	0	99156.072	99156.071	-0.001
9	0	110168.823	110168.814	-0.009
12	0	143197.757	143197.748	-0.009
15	0	176209.641	176209.691	+0.050
16	0	187209.277	187209.219	-0.058
18	0	209200.725	209200.723	-0.002
19	0	220192.348	220192.408	+0.060
20	0	231181.211	231181.190	-0.021
27	0	308009.147	308009.138	-0.009
8	1	98522.943	98522.952	+0.009
9	1	109465.332	109465.341	+0.009
12	1	142283.228	142283.200	-0.028
16	1	186013.252	186013.195	-0.057
20	1	229703.597	229703.630	+0.033
8	2	97891.179	97891.197	+0.018
9	2	108763.371	108763.384	+0.013
12	2	141370.596	141370.622	+0.026
16	2	184819.762	184819.748	-0.014
8	3	97260.822	97260.806	-0.016



CsF: $J = 12 \rightarrow 13$, $v = 0$



CsF: $J = 12 \rightarrow 13$, $v = 1$



CsF: $J = 12 \rightarrow 13$, $v = 2$

(a). The vibrational state populations are in the ratio of 44 to 24 to 14.



Rb^{85}F : $J = 14 \rightarrow 15$, $v = 0$



Rb^{87}F : $J = 15 \rightarrow 16$, $v = 0$

The bottom trace shows the marker.

(b). The percentages of Rb^{85} and Rb^{87} are 72.2% and 27.8% respectively.

Figure 4. Oscilloscope Presentations Comparing Line Strengths.



(a). NaF: $J = 5 \rightarrow 6$, $v = 0$
The vapor temperature is about 1000°C , and
the linewidth approximately 200kc/sec .



(b). KF: $J = 7 \rightarrow 8$, $9 \rightarrow 10$, $11 \rightarrow 12$; $v = 0$
This harmonic series has a klystron frequency
separation of 4Mc/sec between lines.



(c). CsF: $J = 27 \rightarrow 28$, $v = 0$
This is the highest frequency measured
at $308,009.147\text{ Mc/sec}$.



(d). Li^7F : $J = 2 \rightarrow 3$, $v = 0$
Lithium fluoride has the weakest
lines because of dimerization.

Figure 5. Other Oscilloscope Presentations.

for the first time (Table X).

Rubidium fluoride. Both of rubidium fluoride's two isotopes Rb^{87}F and Rb^{85}F have been measured here. Their transitions are listed in Tables V and VI, respectively. Because Rb^{85}F is approximately three times more abundant than Rb^{87}F , the Rb^{85}F transitions were stronger, and hence more transitions of this isotopic species were measured. Oscilloscope traces of comparable transitions of these two isotopic species appear in Figure 4(b).

Lew et al., (1958) have measured the Rb^{85}F , $J = 0 \rightarrow 1$ transition in the $v = 0, 1$, and 2 states by the molecular beam electric resonance method. They measured the Rb^{87}F , $J = 0 \rightarrow 1$ transition only in the $v = 0$ state. Their quoted errors on the measurements vary from 5 to 10 kc/sec at a frequency of about 12 Gc/sec. The present measurements have errors within at most, 75 kc/sec, and averaging 30 kc/sec at frequencies from 100 to 300 Gc/sec. Consequently the relative errors of the two methods are of the same magnitude, with this experiment having an edge by a factor of about two. The values of Y_{01} , Y_{11} , and Y_{21} gratifyingly agree to within the errors of both determinations (see Table XI). These constants, as determined by this experiment, show an error limit improvement by a factor of about three.

Potassium fluoride. This salt gave the most experimental difficulty of the three deliquescent salts CsF , RbF , and KF . The first attempt to measure potassium fluoride was a catastrophe because the hydrogen fluoride from

Table V
Transition Frequencies of Rb⁸⁷F

J	v	Measured frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
8	0	112771.005	112771.000	-0.005
13	0	175370.295	175370.343	+0.048
14	0	187883.001	187882.959	-0.042
15	0	200392.725	200392.712	-0.013
17	0	225402.856	225402.867	+0.011
8	1	111958.326	111958.324	-0.002
14	1	186528.036	186528.037	+0.001
17	1	223776.580	223776.579	-0.001
14	2	185179.061	185179.060	-0.001

Table VI
Transition Frequencies of Rb^{85}F

J	v	Measured frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
7	0	100 667.499	100 667.475	-0.024
8	0	113 246.036	113 245.988	-0.048
10	0	138 397.633	138 397.612	-0.021
14	0	188 673.841	188 673.842	+0.001
15	0	201 236.085	201 236.145	+0.060
17	0	226 351.246	226 351.296	+0.050
20	0	263 997.537	263 997.488	-0.049
23	0	301 607.210	301 607.207	-0.003
7	1	99 940.248	99 940.231	-0.017
8	1	112 427.805	112 427.846	+0.041
14	1	187 310.446	187 310.370	-0.076
15	1	199 781.745	199 781.797	+0.052
17	1	224 715.208	224 715.211	+0.003
14	2	185 952.831	185 952.830	-0.001

Table VII
Transition Frequencies of KF

J	v	Measured frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
5	0	100 275.855	100 275.861	+0.006
6	0	116 983.272	116 983.230	-0.042
7	0	133 688.189	133 688.165	-0.024
8	0	150 390.287	150 390.318	+0.031
9	0	167 089.327	167 089.342	+0.015
10	0	183 784.850	183 784.887	+0.037
11	0	200 476.636	200 476.608	-0.028
13	0	233 847.189	233 847.182	-0.007
5	1	99 440.820	99 440.838	+0.018
6	1	116 009.004	116 009.039	+0.035
7	1	132 574.885	132 574.807	-0.078
9	1	165 697.627	165 697.653	+0.026
5	2	98 610.756	98 610.773	+0.017
6	2	115 040.649	115 040.633	-0.016

the reaction $\text{KF} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{HF}$ etched the glass components and polluted the pump oil. Furthermore, the relatively insoluble KOH clogged the oven. Once these difficulties were solved, however, fourteen lines were measured in three vibrational states. Figure 5(b) shows a harmonic series of the 4th, 5th, and 6th harmonics at frequencies of 133,688.189; 167,089.327; and 200,476.636 Mc/sec, respectively. This picture was taken with the reversing switch on reverse and therefore with the frequency increasing to the left. The klystron frequencies of the higher harmonics occur at succeeding lower frequencies because of centrifugal distortion. Such a harmonic series reduces the search time and therefore is a significant help considering the limited vapor generation time available for this experiment. There are five transitions measured for this harmonic series at a klystron frequency centered about 33,417 Mc/sec. The third and seventh harmonics are off the picture to the left and right of Figure 5(b). They were not tuned in well enough to be seen clearly when these three lines were in tune and photographed.

Green and Lew (1960) measured KF by the molecular beam electric resonance method. The constants Y_{01} , Y_{11} , and Y_{21} as determined by their measurements agree very well with the present measurements (Table XI).

Sodium fluoride. Sodium fluoride was the most difficult salt to vaporize, as an oven temperature of almost 1000°C was required. A compensating property is that it is not hygroscopic; hence the cumbersome dry box

Table VIII
Transition Frequencies of NaF

J	v	Measured frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
3	0	104 229.592	104 229.599	+0.007
4	0	130 280.736	130 280.738	+0.002
5	0	156 327.693	156 327.702	+0.009
6	0	182 369.676	182 369.656	-0.020
9	0	260 457.113	260 457.116	+0.003
3	1	103 147.626	103 147.611	-0.015
4	1	128 928.204	128 928.256	+0.052
5	1	154 704.785	154 704.729	-0.056
6	1	180 476.178	180 476.196	+0.018
3	2	102 076.572	102 076.571	-0.001

operation could be bypassed. The transitions listed in Table VIII were measured in three vibrational states. One transition is pictured in Figure 5(a).

Bauer and Lew (1960) measured sodium fluoride by the molecular beam electric resonance method. At the beginning of their work no accurate value of ω_e for NaF existed. In order to estimate D_e to reduce their data, they needed a good value of ω_e . Consequently, in a separate experiment Ritchie and Lew (1963) measured ω_e and $\omega_e x_e$ for NaF. Their value of ω_e , the best to date, agrees well within both our stated errors to the value determined from the D_e term measured by this experiment (see Table XIII). The values of Y_{01} , Y_{11} , and Y_{21} (Table XI) are slightly outside the stated errors, however.

Lithium fluoride. Lithium fluoride has the two isotopes Li^7F and Li^6F , the first of which is much the more plentiful. Previously only the Li^6F isotope had been studied by microwave techniques. Wharton et al., (1963) chose isotopically pure Li^6F^{19} over the more abundant Li^7F because of the smallness of the Li^6 nuclear electric quadrupole interaction. This present study is the first microwave experiment on the Li^7F molecule of which the author is aware. Because of the large B_e value, there are only two J transitions within the range of this spectrometer. A glance at Table III shows that the absorption coefficient is quite small, dimerization is very high, and the higher vibrational states are only lightly populated. These factors combine to indicate why lithium fluoride is very

Table IX
Transition frequencies of $\text{Li } ^7\text{F}$

J	v	Measured frequency (Mc/sec)	Calculated frequency (Mc/sec)	Difference (Mc/sec)
1	0	160 096.288	160 096.287	-0.001
2	0	240 123.469	240 123.469	+0.000
1	1	157 701.445	157 701.455	+0.000
2	1	236 530.480	236 530.479	-0.001
1	2	155 346.420	155 346.419	-0.001

Table X
Measured Rotational Constants
and their Errors

Molecule	Y_{01} (Mc/sec)	$-Y_{11}$ (Mc/sec)	Y_{21} (Mc/sec)	$-Y_{02}$ (kc/sec)	Y_{12} (kc/sec)
CsF	5 527.265 ± 0.001	35.248 ± 0.002	0.038 ± 0.001	6.046 ± 0.001	-0.009 ± 0.002
Rb ⁸⁷ F	6 288.988 ± 0.003	45.338 ± 0.004	0.099 ± 0.001	7.926 ± 0.006	-0.054 ± 0.006
Rb ⁸⁵ F	6 315.548 ± 0.003	45.652 ± 0.004	0.099 ± 0.001	8.046 ± 0.004	0.011 ± 0.005
KF	8 392.313 ± 0.005	69.999 ± 0.008	0.207 ± 0.002	14.493 ± 0.016	0.007 ± 0.025
NaF	13 097.951 ± 0.007	136.618 ± 0.014	0.684 ± 0.004	34.797 ± 0.045	0.021 ± 0.072
Li ⁷ F	40 329.907 ± 0.150	608.569 ± 0.250	4.98 ± 0.03	343. $\pm 9.$	12. $\pm 4.$

Table XI
Comparison of Measured Rotational Constants

Molecule	Present Y_{01} (Mc/sec)	Previous Y_{01} (Mc/sec)	Present Y_{11} (Mc/sec)
CsF	5 527.265 ± 0.001	5 527.27 ^a ± 0.04	35.247 ± 0.002
Rb ⁸⁷ F	6 288.988 ± 0.003	6 289.002 ^b ± 0.010	45.338 ± 0.004
Rb ⁸⁵ F	6 315.548 ± 0.003	6 315.543 ^b ± 0.009	45.652 ± 0.004
KF	8 392.313 ± 0.005	8 392.309 ^c ± 0.004	69.999 ± 0.008
NaF	13 097.951 ± 0.007	13 097.971 ^e ± 0.003	136.618 ± 0.014
Li ⁷ F	40 329.907 ± 0.150	40 329.987 ^f ± 0.005	608.569 ± 0.250

a. Honig et al., (1954).

b. Lew et al., (1958).

c. Ritchie and Lew, (1964).

Table XI (continued)

Previous Y_{11} (Mc/sec)	Present Y_{21} (Mc/sec)	Previous Y_{21} (Mc/sec)
33.13 ^a ± 0.05	0.038 ± 0.001	0.009 ^a ± 0.012
45.350 ^b ± 0.017	0.099 ± 0.001	0.094 ^b ± 0.007
45.638 ^b ± 0.017	0.099 ± 0.001	0.094 ^b ± 0.007
69.991 ^d ± 0.010	0.207 ± 0.002	0.204 ^d ± 0.005
136.665 ^e ± 0.005	0.684 ± 0.004	0.700 ^e ± 0.001
608.154 ^f $+0.005$	4.977 $+0.030$	4.633 ^f $+0.005$

d. Green and Lew, (1960).

e. Bauer and Lew, (1963).

f. Wharton et al., (1963) (mass ratio conversions of their Li^6F constants)

difficult to measure.

The errors of the five lines (Table IX) measured for Li^7F are computed in a manner slightly different from the method described in Chapter II. Since there are only five transitions, there is no redundancy in the measurements. The fit indicated in Table IX is therefore unrealistic, especially in light of the fact that the dispersion of these measurements is larger than for the other molecules. Especially, there is a large dispersion on the $J = 1 \rightarrow 2$, $v = 2$ transition, the weakest one measured. Consequently, each forward and reverse measurement is considered as one measurement of the several for each transition. The dispersion for the measurement with the largest deviation from the average for a transition is considered to be the difference d_i for each measurement of that transition. Thereafter these d_i 's are treated as described in Chapter II.

Since no direct microwave comparison could be made on Li^7F measurements, a comparison with Li^6F constants converted by mass ratios according to Equation (37) is made (see Table XI). The Y_{01} constants agree within experimental error. The Y_{11} terms agree within twice the error, but the Y_{21} terms differ by ten times the stated error. However, it must be recalled that the relations of Equation (37) are not meant to be exact relationships.

Calculated Dunham Constants. The Y_{lm} 's which were not directly measured but which could be calculated with reasonable error limits appear in Table XII. The Y_{13} value was calculated, but the error limits were much

Table XII

Calculated Dunham Constants

Molecule	Y_{00} (Gc/sec)	Y_{03} (cps x 10^{-3})	Y_{04} (cps x 10^{-3})
CsF	0.596 ± 0.092	-0.214 ± 0.002	-0.0054 ± 0.0004
Rb ⁸⁷ F	-0.830 ± 0.277	-1.404 ± 0.012	-0.0192 ± 0.0018
Rb ⁸⁵ F	2.021 ± 0.249	-1.381 ± 0.008	-0.0041 ± 0.0016
KF	2.144 ± 0.753	-2.895 ± 0.042	-0.0197 ± 0.0116
NaF	3.464 ± 1.153	-12.306 ± 0.179	-0.112 ± 0.066
Li ⁷ F	34. $\pm 14.$	807. $\pm 110.$	35. $\pm 37.$
Li ⁶ F	15.640 ± 0.575	1299.9 ± 2.2	3.1 ± 1.7

a. Calculated from the data of Wharton et al., (1963).

greater than the value of the constant itself; therefore it is not listed. The Y_{00} value represents a correction to the zero point vibrational energy. The inconsistency in the sign of the Rb^{87}F Y_{00} is not understood.

The Y_{03} values listed in Table XII are unchanged from the ones used in a second iteration. The equation used to calculate the Y_{03} or H_e correction term is

$$Y_{03} = 2 \frac{D_e}{3\omega_e^2} (12 B_e - \alpha_e \omega_e) , \quad (52)$$

which may be derived from Equations (26) and (28). The correction to the line frequencies by the Y_{03} term multiplied by the appropriate coefficient is within the dispersion of the frequency measurements. There is usually no correction to low J transition frequencies, and the higher J transition frequencies are corrected by only a few kilocycles.

The Y_{04} term in some cases has an error larger than the term itself, and its value is smaller by two orders of magnitude than Y_{03} . For this reason it was not considered in the frequency equation.

The Vibrational Terms

The vibrational constants ω_e and $\omega_e x_e$ are listed in Table XIII with other values for comparison. The present values are calculated by equations (24) and (34), respectively. All of the ω_e terms agree within the latest and most accurate determinations of this vibrational constant. Except for Li^7F , the values of ω_e from this experiment appear to be

one to two orders of magnitude more accurate than those from infrared techniques.

G.L. Vidale (1960) made some very accurate infrared measurements of Li^7F . However, because of an unresolved ambiguity in the assigned value of the J quantum number, he gave three sets of possible vibrational and rotational constants (Table XIV). He stated that if any of the parameters could be determined by another method, the probable error could be reduced by a factor of ten. The present work shows directly that the third set of Vidale's results (the one he considered much less probable) is the true one. Wharton et al., indirectly showed that Vidale's third less probable set was the correct one by mass ratio conversion of their Li^6F data. Now Vidale's values of ω_e and $\omega_e x_e$ from set M - 2 should be considered the best values available for Li^7F .

The present calculations of $\omega_e x_e$ are consistently higher than the values for CsF, RbF, KF, and NaF of Barrow and Caunt (1953) and Ritchie and Lew (1963) (Table XIII). Rusk (1961) found this same consistency in the difference between his alkali bromide and alkali iodide $\omega_e x_e$ values and the values of Barrow and Caunt. The present Li^7F $\omega_e x_e$ term is not as reliable as that of the other alkali fluorides. Although it lies below the values of Vidale (1960) and of Vasileuskii and Baikov (1961), it agrees within experimental error with the value quoted by the latter.

Table XIII
Vibrational Constants

Molecule	Present ω_e (cm^{-1})	Best Previous ω_e (cm^{-1})	Other values of ω_e (cm^{-1})	
CsF	352.56 ± 0.04	357. ^a $\pm 15.$	385 ^d ,	270 ^e ± 30
Rb ⁸⁷ F	373.74 ± 0.14	378. ^a $\pm 10.$		
Rb ⁸⁵ F	373.27 ± 0.08	378. ^a $\pm 10.$	390 ^d ,	340 ^f ± 68
KF	426.04 ± 0.24	429. ^a $\pm 3.$	405 ^d ,	390 ^g ± 39
NaF	536.10 ± 0.35	536. ^a $\pm 2.$		
Li ⁷ F	922. $\pm 12.$	910.34 ^{b, c}	646 ^h , ± 32	897 ⁱ ± 5
Li ⁶ F		964.07 ^b	756 ^h , ± 38	930 ^j ± 19

a. Ritchie and Lew (1963) (KF and NaF are measurements, RbF and CsF extrapolations).

b. Wharton et al., (1963).

c. Vidale (1960).

d. Barrow and Caunt (1953).

e. Trischka (1949).

f. Hughes and Grabner (1950).

Table XIII (continued)

Rittner's calculated ^k ω_e (cm ⁻¹)	Present ω_e^x (cm ⁻¹)	Previous ω_e^x (cm ⁻¹)
345	-1.62 ±0.01	1.23 ^d
	-2.18 ±0.03	
361	-1.80 ±0.03	1.3 ^d
410	-2.43 ±0.09	1.45 ^d , 2.4 ^a ±0.25
477	-3.83 ±0.14	3.4 ^a ±0.25
773	-5.4 ±1.5	7.90 ^c , 7.3 ⁱ ±0.01 ±0.5
		8.8953 ^b

g. Grabner and Hughes (1950).

h. Braunstein and Trischka (1955).

i. Vasilevskii and Baikov (1961).

j. Moran and Trischka (1961).

k. Rittner (1951).

Table XIV
 Li^7F Comparison with Vidale's Three Sets
of Parameters

Parameter	Present Li^7F	Probable ^a set M	Probable ^a set M-1	Less Prob- able set ^a M-2
$\omega_e(\text{cm}^{-1})$	922.	904.85	907.64	910.34
$\omega_e x_e(\text{cm}^{-1})$	5.4	7.889	7.910	7.929
$\omega_e(\text{cm}^{-1})$	0.020299	0.019556	0.019856	0.020000
$B_e(\text{cm}^{-1})$	1.3454	1.3881	1.3676	1.3468
$r_e(\text{\AA})$	1.563904	1.5397	1.5512	1.5631

a. Vidale (1960).

Potential Coefficients

The potential coefficients a_0 , a_1 , a_2 , and a_3 are calculated according to the equations listed in Chapter II. They appear in Table XV. In Equation (27) ω_e is ~~is~~ in cm^{-1} , B_e is in Mc/sec , and the value of c is taken to be 2.99793×10^{10} cm/sec (Dumond and Cohen, 1958). Therefore the units of a_0 are cm^{-1} , while the remaining coefficients are dimensionless. There is substantial agreement with the summary of these coefficients based on previous data given by Ritchie and Lew (1964) for all the alkali fluorides excluding lithium fluoride. The previous calculations were seriously limited by inaccurate values of ω_e . It is believed that the present calculations of ω_e have enabled the best available potential coefficient computations to be made.

Moments of Inertia and Internuclear Distances

Table XVI gives the internuclear distance r_e and the values of molecular constants needed to calculate r_e . Table XVII compares different values of r_e . Green and Lew (1960) found Krasnov's computation of r_e to be the most reliable of several theoretical methods. Such a computation appears in Table XVII for comparison with the measured values.

The B_e term is calculated by an iteration procedure according to Equation (16); β_{01} comes from Equation (17). Then I_e and r_e are

Table XV
Potential Coefficients

Molecule	a_0 ($\text{cm}^{-1} \times 10^{-5}$)	a_1	a_2	a_3
CsF	1.6855 ± 0.0003	-3.0324 ± 0.0003	5.65 ± 0.04	-7.2 ± 0.4
Rb ⁸⁷ F	1.6646 ± 0.0013	-3.1406 ± 0.0010	5.40 ± 0.11	-2.2 ± 1.1
Rb ⁸⁵ F	1.6535 ± 0.0007	-3.1347 ± 0.0007	6.58 ± 0.10	-11.4 ± 1.0
KF	1.6210 ± 0.0018	-3.1157 ± 0.0014	6.34 ± 0.23	-9.6 ± 2.2
NaF	1.6445 ± 0.0021	-3.1331 ± 0.0016	6.43 ± 0.23	-9.2 ± 2.1
Li ⁷ F	1.5802 ± 0.0414	-2.7239 ± 0.0233	6.60 ± 0.89	-17.2 ± 8.3
Li ⁶ F ^a	1.5399 ± 0.0005	-2.7006 ± 0.0003	5.18 ± 0.03	-8.5 ± 0.3

a. Calculated from the data of Wharton et al., (1963).

Table XVI
Molecular Constants

Molecule	B_e (Mc/sec)	β_{01}	I_e (amu-Å ²)	r_e (Å)
CsF	5527.266 ±0.002	-0.7 ±1.0	91.4715 ±0.0035	2.345462 ±0.000045
Rb ⁸⁷ F	6288.957 ±0.007	16.1 ±2.8	80.3929 ±0.0031	2.270450 ±0.000044
Rb ⁸⁵ F	6315.576 ±0.006	-14.2 ±2.6	80.0540 ±0.0031	2.270435 ±0.000043
KF	8392.349 ±0.009	-10.0 ±5.8	60.2438 ±0.0023	2.171554 ±0.000042
NaF	13098.042 ±0.014	-10.5 ±5.7	38.6002 ±0.0015	1.926032 ±0.000037
Li ⁷ F	40333.798 ±0.300	-45.3 ±19.0	12.5351 ±0.0005	1.563861 ±0.000033
Li ⁶ F ^a	45232.563 ±0.005	-15.8 ±0.7	11.1775 ±0.0004	1.563904 ±0.000030

a. Calculated from the data of Wharton et al., (1963).

Table XVII
Comparison of Internuclear Distances^a

Molecule	Present (Å)	Other (Å)	Krasnov ^h (Å)
CsF	2.34546 (4)	2.3453 (1) ^b	2.345
Rb ⁸⁷ F	2.27045 (4)	2.27031 (5) ^c	2.259
Rb ⁸⁵ F	2.27043 (4)	2.27031 (5) ^c	2.259
KF	2.17155 (4)	2.17146 (5) ^d	2.166
NaF	1.92603 (4)	1.92595 (6) ^e	1.917
Li ⁷ F	1.56386 (3)	1.563 (6) ^f	1.584
Li ⁶ F		1.56389 (5) ^g	1.584

a. The figures in parentheses indicate the uncertainty in the last digit.

b. Honig et al., (1954).

c. Lew (1964) (a correction to the value given by Lew et al., (1958)).

d. Ritchie and Lew (1963) (a correction to the value of Green and Lew (1960)).

e. Bauer and Lew (1963).

f. Vidale (1960).

g. Wharton et al., (1963).

h. Green and Lew (1960).

obtained by Equations (32) and (33) respectively. The value of the reduced mass used in Equation (33) is listed in Table XVIII along with the atomic masses from which the reduced masses are calculated. There is agreement within the stated errors on CsF, KF, and NaF. The rubidium fluoride values disagree just slightly outside the error limits in the fourth place to the right of the decimal. Vidale's best r_e value of $1.545 \text{ \AA}$ for Li^7F is known to be in error since the correct set of data was not used. The set now shown to be correct gives the value of $1.5631 \text{ \AA}$, which is in excellent agreement with the present value. It should be noted that the internuclear distances of the rubidium and lithium isotopic species agree almost exactly.

Mass Ratios

The mass ratios of the rubidium and lithium isotopes and their errors were derived from Equations (41) and (42). However, Y_{01} values were used instead of the less accurate B_e values. The present data for Y_{01} was used for Rb^{87}F , Rb^{85}F , and Li^7F , but the data of Wharton et al., was used for Li^6F . The atomic masses of Johnson, Quisenberry, and Nier (1958) listed in Table XVIII were used to calculate the reduced mass appearing in the same table. This reduced mass is needed in Equation (40). Finally the mass ratios appear in Tables XIX and XX with other values for comparison.

Table XVIII
Atomic and Reduced Masses

	Atomic ^a mass (amu)	Fluoride molecule reduced mass (amu)
F	19.0044431 ±0.0000024	
Cs	132.94739 ±0.00007	16.627578
Rb ⁸⁷	86.93694 ±0.00017	15.595304
Rb ⁸⁵	84.93902 ±0.00006	15.529776
K	38.9761002 ±0.0000018	12.775303
Na	22.9970910 ±0.0000021	10.405498
Li ⁷	7.018232 ±0.000006	5.125437
Li ⁶	6.017034 ±0.000005	4.570089

a. Johnson, Quisenberry, and Nier (1958).

Table XIX
Mass Ratio of Rubidium Isotopes

Method	Molecule	$\text{Rb}^{85}/\text{Rb}^{87}$
Present	RbF	0.9769987 (55)
Present ^b	RbCl	0.9770086 (112)
Present ^c	RbI	0.9770162 (93)
Hot Cell ^d	RbI	0.9770177 (45)
Hot Cell ^d	RbBr ⁷⁹	0.9770146 (55)
MBER ^e	RbF	0.9770148 (52)
Mass spectroscopy ^f		0.9770187 (1100)

a. The error in the last significant digits appears in parentheses.

b. Clouser and Gordy, (1964).

c. Rusk and Gordy, (1962).

d. Honig et al., (1954).

e. Lew et al., (1958).

f. Ratio of masses listed in Table XVIII.

Table XX

Mass Ratio of Lithium Isotopes

Method	Molecule	Li^6/Li^7
Combination present and MBER ^b	LiF	0.8573359 (51)
Hot cell ^c	LiI	0.8573423 (20)
Mass Spectroscopy ^d		0.8573433 (10)

a. The error in the last significant digits appears in parentheses.

b. Molecular beam electric resonance data for Li^6F from Wharton et al., (1963).

c. Honig et al., (1954).

d. Ratio of masses given in Table XVIII.

CONCLUSIONS

This dissertation has described the results of measurements in a region of the spectrum never before broached for the alkali fluorides. The spectrometer has proven most fruitful in that it has obtained new results and confirmed and improved parameters from three other types of spectrometers. This report on the alkali fluorides completes the alkali halide series on the present spectrometer, with the exception of lithium chloride. However, measurements on $\text{Li}^7\text{Cl}^{35}$ and $\text{Li}^7\text{Cl}^{37}$ have recently been made here and a paper will soon be published. (Pearson and Gordy, to be published)

Previously Rusk tried unsuccessfully to measure LiF , and Clouser attempted LiCl with similar results. Their difficulty was directly attributable to the heavy dimerization of these two molecules. The new oven made the recent successes possible. The temperature could be raised quickly after vapor generation began to reduce the dimer concentration and increase the line strength.

Two courses are being considered for future work on the high temperature molecular beam microwave spectrometer. The first and most

important course would require a hotter oven and greater sensitivity in the submillimeter region for oxide and hydride study. Secondly, the present increased sensitivity of the spectrometer for higher frequencies would permit a valuable extension of the alkali bromide and iodide measurements.

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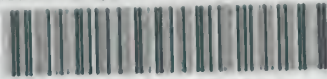
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